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International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C10L 1/14, 10/04</b>	<b>A1</b>	(11) International Publication Number: <b>WO 99/61562</b> (43) International Publication Date: <b>2 December 1999 (02.12.99)</b>
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(21) International Application Number: **PCT/EP99/03306**

(22) International Filing Date: **13 May 1999 (13.05.99)**

(30) Priority Data:  
**9810994.5** **22 May 1998 (22.05.98)** **GB**

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(81) Designated States: **AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).**

**Published**  
*With international search report.*

(54) Title: **ADDITIVES AND OIL COMPOSITIONS**

(57) Abstract

**Oils having improved low temperature properties and additives for use therein.**

## ADDITIVES AND OIL COMPOSITIONS

5 This invention relates to improved oil compositions and improved additives therefor, in particular to fuel oil compositions having improved low temperature flow and especially filterability properties, and to additives enhancing a variety of fuel properties and providing operational advantages for fuel manufacturers and users.

10 Many oil, and particularly fuel oil, compositions suffer from the problem of reduced flowability and/or filterability at low temperatures, due to the precipitation of the heavier alkanes (and particularly n-alkanes) inherent in such oils. This problem of alkane crystallisation at low temperatures is well known in the art. Additive  
15 solutions to this problem have been proposed for many years, in particular, copolymers of ethylene and vinyl esters such as vinyl acetate or vinyl propionate have been successfully used in commercial applications and are well documented in the patent literature.

20 The problem of poor low temperature filterability has conventionally been measured by the Cold Filter Plugging Point ("CFPP") test, which determines the ease with which fuel moves under suction through a filter grade representative of field equipment. The determination is repeated periodically during steady cooling of the fuel sample, the lowest temperature at which the minimum acceptable level  
25 of filterability is still achieved being recorded as the "CFPP" temperature of the sample. The details of the CFPP test and cooling regime are specified in the European Standard method EN116. The CFPP test is acknowledged as a standard bench test for determining fuel performance and, as such, has been adopted in many national fuel specifications. Such specifications set a number of  
30 minimum technical requirements for fuels of particular grades, so establishing a minimum quality level below which fuels are not considered technically "fit for purpose".

flexibility in meeting the required low temperature aspects of the fuel specification. The material can, when formulated within an additive composition or concentrate further comprising a polar nitrogen-containing additive, also improve the overall physical compatibility of the additive blend and accordingly reduce the need for  
5 high quantities of polar solvent.

Recently, the advent of more stringent fuel oil sulphur specifications has led to a deterioration in fuel oil lubricity.

10 Environmental concerns have led to a need for fuels with reduced sulphur content, especially diesel fuel and kerosene. However, the refining processes that produce fuels with low sulphur contents also lower the content of other components in the fuel that contribute to its lubricity, for example, polycyclic aromatics and polar compounds. The result, has been an increase in reported  
15 failures of fuel pumps in diesel engines using low-sulphur fuels, the failure being caused by wear in, for example, cam plates, rollers, spindles and drive shafts.

This problem may be expected to become worse in future because, in order to meet stricter requirements on exhaust emissions generally, higher pressure fuel  
20 pumps and systems, including in-line, rotary and unit injector systems, are being introduced, these being expected to have more stringent lubricity requirements than present equipment.

At present, a typical sulphur content in a diesel fuel is about 0.05% by weight. In  
25 Europe maximum sulphur levels are expected to be reduced to 0.035%; in Sweden grades of fuel with levels below 0.005% (Class 2) and 0.001% (Class 1) are already being introduced. A fuel oil composition with a sulphur level below 0.05% by weight is referred to as a low sulphur fuel.

30 The co-additive material of this invention can also provide enhanced fuel lubricity, reducing or eliminating the need for a conventional lubricity additive whilst enabling the desired (or specified) fuel lubricity performance to be achieved.

Other advantages of the invention will become apparent from the following  
35 description.

In a second aspect, the invention provides an additive concentrate comprising either the additive composition of the first aspect, or (a), (b) and (c) as defined in the first aspect, in admixture with a compatible solvent therefore.

5

In a third aspect, the invention provides a fuel oil composition comprising fuel oil and either the additive or concentrate of the first or second aspect, or (a), (b) and (c) as defined in the first aspect.

10 In a fourth aspect, the invention provides a process for the manufacture of the fuel oil composition of the third aspect, comprising:

(i) obtaining a fuel oil, and

15 (ii) blending therewith either the additive or concentrate composition of any preceding claim, or the components (a), (b) and (c) as defined in any preceding claim.

20 In a fifth aspect, the invention provides the use of the reaction product (b) as defined in the first aspect as an additive for a fuel oil composition comprising (a) and (c) as defined in the first aspect.

In a sixth aspect, the invention provides the use of the additive or concentrate composition of the first or second aspect in fuel oil.

25

In a seventh aspect, the invention provides a method of operating an oil refinery or fuel oil manufacturing facility comprising:

30 (i) manufacturing a fuel oil with low temperature properties insufficient to meet the required technical specification for that oil,

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- $R^1$  represents hydrogen or a moiety bearing at least one hydrocarbyl group, and
  - $R^3$  represents a COOH or SO<sub>3</sub>H group or derivative thereof, and
- 5        wherein X and  $R^1$  in reactants (ii) and (iii) may be the same or different.

Such embodiments of (b) show excellent performance and provide, in particular, excellent CFPP and lubricity enhancement. Most preferably, such embodiments  
10 of (b) are also combined with the hydrocarbyl amine to give co-additives having the optimum balance of properties, including excellent CFPP and wax anti-settling enhancement, good lubricity performance, especially in fuels having sulphur contents of less than 0.05% by weight, such as 0.035% S by weight or less, and good compatibility with (a) and (c).

15        The various aspects of the invention will now be described in more detail as follows:

### Additive Composition Aspects of the Invention

20

#### (a) The Ethylene Polymer(s)

Each polymer may be a homopolymer or a copolymer of ethylene with another unsaturated monomer. Suitable co-monomers include  
25 hydrocarbon monomers such as propylene, n- and i- butylene and the various  $\alpha$ -olefins known in the art, such as decene-1, dodecene-1, tetradecene-1, hexadecene-1 and octadecene-1.

30

Preferred co-monomers are unsaturated ester or ether monomers, with ester monomers being more preferred.

Within the meaning of this specification, "copolymer" refers to a polymer obtained from two or more different co-monomers.

Most preferably, (a) comprises an ethylene vinyl acetate or ethylene vinyl propionate copolymer, or a mixture thereof, or a terpolymer of ethylene and two vinyl esters, each giving rise to polymer units corresponding to the above formula. Particularly preferred are terpolymers of ethylene, vinyl acetate and a third unsaturated ester monomer, for example, selected from vinyl propionate, vinyl 2-ethyl hexanoate, or vinyl versatate.

#### (b) The Product of the Condensation Reaction

Reactant (i) comprises one or more aldehydes or ketones or reactive equivalents thereof. By "reactive equivalent" is meant a material which generates an aldehyde under the conditions of the condensation reaction or a material which undergoes the required condensation reaction to produce moieties equivalent to those produced by an aldehyde. Typical reactive equivalents include oligomers or polymers of the aldehyde, acetals, or aldehyde solutions.

The aldehyde may be a mono- or di- aldehyde and may contain further functional groups, such as -COOH or -SO<sub>3</sub> groups capable of post-reaction in the product (b). The aldehyde preferably contains 1-28 carbon atoms, more preferably 1-20, such as 1-12, carbon atoms. The aldehyde is preferably aliphatic, such as an alkyl or alkenyl. The aldehyde (i) may comprise a mixture of different aldehydes.

Particularly preferred reactants (i) are formaldehyde, acetaldehyde, the butyraldehydes and substituted analogues or reactive equivalents thereof. Formaldehyde and glyoxylic acid (or pyruvic acid) are particularly preferred.

Reactant (ii) preferably comprises one or more compounds wherein each aromatic moiety bears one substituent of the formula -XR<sup>1</sup>. More preferably, (ii) bears one substituent of the formula R<sup>2</sup> and most preferably, also one substituent of the formula -XR<sup>1</sup>. X is preferably oxygen.

group, which may be branched or preferably straight chain. The hydrocarbyl group in  $R^1$  may be bonded directly to the oxygen or sulphur atom (represented by X in the formula  $-XR^1$ ) or may be bonded indirectly by means of a functional group, for example on ester, ether, peroxide, anhydride or polysulphide linkage.

Preferably, where  $R^1$  is hydrocarbyl, the hydrocarbyl group in  $R^1$  contains 8-40 carbon atoms, more preferably 12-24 carbon atoms, such as 12-18 carbon atoms.

Most preferably,  $R^1$  is hydrogen.

$R^2$  may independently represent those hydrocarbyl groups contemplated as forming part of the moiety  $R^1$ , although typically  $R^1$  and  $R^2$  (where both are present) will on any one aromatic moiety, will be different from each other, and may be the same or different on different aromatic moieties.

Preferably,  $R^2$  is an alkenyl or, more preferably, alkyl group, most preferably containing less than 18 carbon atoms. It has been found that where  $R^2$  contains 18 or more carbon atoms and is linear, the effectiveness of the product (c) as a low temperature performance enhancing additive is reduced. More preferably,  $R^2$  is a branched chain group, preferably an alkyl group. Most preferred embodiments of  $R^2$  include branched chain alkyl groups containing less than 16 carbon atoms, for example 4 to 16 carbon atoms, such as groups containing 8, 9, 12 or 15 carbon atoms. Groups containing 9 carbon atoms are most preferred. Minor amounts of short chain alkyl groups (e.g. 4 carbons or less) may be present.

Reactant (ii) may be formed by the Friedel-Crafts reaction, in the presence of a suitable catalyst, such as boron trifluoride and its complexes with ether, phenol, hydrogen fluoride, and such as aluminium chloride or bromide. In this reaction, under conditions well known in the art, the aromatic moiety (substituted with group  $-XR^1$ ) is reacted with the appropriate pre-cursor of the substituent  $R^2$  (such as the corresponding  $R^2$  halide) to form the desired reactant (ii).



It is believed that the compositions of this invention contain bridges derived from the organic residue of the aldehyde linking the organic residues of the aromatic compound. Thus, when (i) is formaldehyde, methylene bridges are formed. The invention, however, is in no way intended to be limited by reference to such bridges. The formation of bridges may lead to linear or cyclic macromolecules containing units of (ii) and optionally (iii).

An example of the condensation product was prepared by heating a stirred mixture of 40g branched-nonylphenol, 5.75g of 95% paraformaldehyde and 0.1g p-toluene sulphonic acid monohydrate in 50 ml xylene to 80-85°C for two hours, followed by reflux at 150-155°C for six hours, the water of reaction being continuously removed via a Dean and Stark receiver. The product had an Mn of 2050 and an Mw of 2940.

One product (c) typically has a number-average molecular weight (Mn), as measured by GPC against polystyrene standards, in the range of 500 to 10,000, preferably 500 to 5,000, more preferably 500 to 2,500. The molecular weight distribution (Mw/Mn - wherein both Mn and Mw are measured by GPC) is advantageously in the range of 1 to 2, more preferably 1 to 1.5, such as 1.3 to 1.4.

Preferably, the product (b) is formed from a reactant (ii) which comprises at least one aliphatic hydrocarbyl-substituted phenol, such as branched chain C<sub>9</sub> or C<sub>15</sub> alkyl phenol.

The product (b) may be combined with at least one amine bearing at least one hydrocarbyl substituent. Such combination may be purely by admixture, but is preferably by physical or chemical association or complexation. More preferably, (b) is reacted with at least one amine, more preferably to form the amine salt derivative thereof.

The amine may contain three or four, or preferably one or two, hydrocarbyl substituents. Amines with two substituents are most preferred. The substituents may be aliphatic, for example alkyl or alkenyl groups, and may contain up to 40 carbon atoms, for example up to 28 carbon atoms.

nonylphenol-formaldehyde-salicylic acid condensation product had an Mn of 1960 and an Mw of 2900.

5 Alternatively, (b) may be obtained by the reaction of (i) and (ii) to form a condensation product, followed by further reaction with (iii) to form a product wherein the units derived from (iii) are for example predominantly terminally positioned. An example was prepared by heating a stirred mixture of 40g nonylphenol, 5.5g of 95% paraformaldehyde and 0.1g p-toluene sulphonic acid monohydrate in 50 ml xylene to 80-85°C for four  
10 hours, followed by addition thereto of 3.1g salicylic acid reflux for five hours at 152-158°C. The water of reaction was continuously removed via a Dean and Stark receiver. The resulting nonyl-phenol-formaldehyde-salicylic acid condensation product had an Mn of 1540 and an Mw of 2200.

15 Alternatively, (b) may be obtained by the reaction of (i) and (ii) to form a condensation product, followed by partial carboxylation or sulphonation such that some units derived from (ii) are converted *in situ* into units having structures corresponding to those of (iii). Such products also fall within the scope of this invention.

20 More preferably, the products obtainable from reaction of (i), (ii) and (iii) are combined with at least one amine, as described above. In such products, the amine is preferably reacted with the substituents of the formula -R<sup>3</sup>, e.g. the -COOH or -SO<sub>3</sub>H groups, so as to form the amine salt derivatives thereof; although salt formation may additionally occur via any -  
25 OH substituents.

30 Most preferred as the product (b) are embodiments obtainable from at least one alkyl phenol (i) wherein the alkyl substituent contains no more than 15 carbon atoms, formaldehyde or a reactive equivalent thereof, and (iii) salicylic acid, and wherein the amine is an alkyl or dialkyl amine, preferably as described above and more preferably selected from dihydrogenated tallowamine, dicocoamine, and mixtures thereof.

35 The additive composition of the first aspect is obtainable, and preferably obtained, by admixture of the components (a), (b) and (c). The admixture may for example be achieved by blending together the components in a suitable vessel, or for

groups may contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group. Examples include keto, halo, hydroxy, nitro, cyano, alkoxy and acyl. If the hydrocarbyl group is substituted, a single (mono) substituent is preferred.

5 Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, sulphur, and, preferably, oxygen.

15 The polar nitrogen compound may comprise one or more amino or imino substituents. More especially, the or each amino or imino substituent is bonded to a moiety via an intermediate linking group such as  $-\text{CO}-$ ,  $-\text{CO}_2(-)$ ,  $-\text{SO}_3(-)$  or hydrocarbylene. Where the linking group is anionic, the substituent is part of a cationic group, as in an amine salt group.

20 When the polar nitrogen compound carries more than one amino or imino substituent, the linking groups for each substituent may be the same or different.

Suitable amino substituents are long chain  $\text{C}_{12}-\text{C}_{40}$ , preferably  $\text{C}_{12}-\text{C}_{24}$ , alkyl primary, secondary, tertiary or quaternary amino substituents.

25 Preferably, the amino substituent is a dialkylamino substituent, which, as indicated above, may be in the form of an amine salt thereof; tertiary and quaternary amines can form only amine salts. Said alkyl groups may be the same or different.

30 Examples of amino substituents include dodecylamino, tetradecylamino, cocoamino, and hydrogenated tallow amino. Examples of secondary amino substituents include dioctadecylamino and methylbehenylamino. Mixtures of amino substituents may be present such as those derived from naturally occurring amines. Preferred amino substituents are the secondary hydrogenated tallow amino substituent, the alkyl groups of which are derived from hydrogenated tallow fat and are typically composed of

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- (iv) Heterocyclic compounds such as quinoline, indole, 2:3 dihydroindole, benzofuran, coumarin, isocoumarin, benzothiophen, carbazole and thiodiphenylamine,
- (v) Non-aromatic or partially saturated ring systems such as decalin (i.e. decahydronaphthalene),  $\alpha$ -pinene, cardinene, and bornylene, and
- (vi) Three-dimensional structures such as norbornene, bicycloheptane (i.e. norbornane), bicyclooctane, and bicyclooctene.

Examples of polar nitrogen compounds are described below:

- (i) Amine salts and/or amides of mono- or poly- carboxylic acids or reactive equivalents thereof (e.g. anhydrides), e.g. having 1-4 carboxylic acid groups. Each may be made, for example, by reacting at least one molar proportion of a hydrocarbyl substituted amine with a molar proportion of the acid or its anhydride.

When an amide is formed, the linking group is  $-\text{CO}-$ ; when an amine salt is formed, the linking group is  $-\text{CO}_2(-)$ .

The acid may be cyclic or non-cyclic. Examples of cyclic moieties are those where the acid is cyclohexane 1,2-dicarboxylic acid; cyclohexane 1,2-dicarboxylic acid; cyclopentane 1,2-dicarboxylic acid; and naphthalene dicarboxylic acid. Generally, such acids have 5-13 carbon atoms in the cyclic moiety. Preferred such cyclic acids are benzene dicarboxylic acids such as phthalic acid, isophthalic acid, and terephthalic acid, and benzene tetracarboxylic acids such as pyromellitic acid, phthalic acid being particularly preferred. US-A-4,211,534 and EP-A-272,889 describe polar nitrogen compounds containing such moieties.

Examples of non-cyclic acids are those when the acid is a long chain alkyl or alkylene substituted dicarboxylic acid such as a succinic acid, as described in US-A-4,147,520 for example.

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- (a) Ethylenically unsaturated when A and B may be alkyl, alkenyl or substituted hydrocarbyl groups or,
- (b) Part of a cyclic structure which may be aromatic, polynuclear aromatic or cyclo-aliphatic,

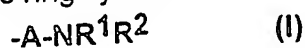
it is preferred that X-R<sup>1</sup> and Y-R<sup>2</sup> between them contain at least three alkyl, alkoxyalkyl or polyalkoxyalkyl groups.

Multicomponent additive systems may be used and the ratios of additives to be used will depend on the fuel to be treated.

(iii) Amines or diamine salts of:

- (a) A sulphosuccinic acid,
- (b) An ester or diester of a sulphosuccinic acid,
- (c) An amide or a diamide of a sulphosuccinic acid, or
- (d) An ester amide of a sulphosuccinic acid.

(iv) Chemical compounds comprising or including a cyclic ring system, the compound carrying at least two substituents of the general formula (I) below on the ring system:



where A is an aliphatic hydrocarbyl group that is optionally interrupted by one or more hetero atoms and that is straight chain or branched, and R<sup>1</sup> and R<sup>2</sup> are the same or different and each is independently a hydrocarbyl group containing 9-40 carbon atoms optionally interrupted by one or more hetero atoms, the substituents being the same or different and the compound optionally being in the form of a salt thereof.

Preferably, A has from 1-20 carbon atoms and is preferably a methylene or polymethylene group.

5 The most preferred polar nitrogen compounds are those wax anti-settling additives comprising the amides and/or amine salts, or mixtures thereof, of aromatic or aliphatic polycarboxylic acid (or reactive equivalents thereof) and alkyl or dialkyl amines, such as those formed from the following:

- 10 (i) Benzene dicarboxylic acids (or anhydrides thereof), such as phthalic anhydride [which isomers?],
- (ii) Alkylene di- or polyamine tetraacetic or tetra propionic acids, such as EDTA (Ethylene Diamine Tetraacetic Acid), and
- (iii) Alkyl or alkenyl substituted succinic acids.

15 The preferred amines include dialkyl amines having 10-30, preferably 12-20 carbon atoms in each alkyl chain, for example dihydrogenated tallow amine or dicocamine, or mixtures thereof.

20 Compounds resulting from the reaction of phthalic anhydride and dialkyl amines, such as those specified above, are most preferred.

### Co-additives

25 The additive composition may additionally comprise one or more co-additives useful in fuel oil compositions. Such co-additives include other cold flow improving additives, such as one or more additives selected for the following classes:

- 30 (i) comb polymers  
(ii) linear ester, ether, ester/ethers and mixtures thereof;  
(iii) non-ethylene hydrocarbon polymers, and  
(iv) hydrocarbylated aromatic compounds.

35 Such co-additives are described in more detail below.

and m and n represent mole ratios, their sum being 1 and m being finite and being up to and including 1 and n being from zero to less than 1, preferably m being within the range of from 1.0 to 0.4, n being in the range of from 0 to 0.6. R<sup>11</sup> advantageously represents a hydrocarbonyl group with from 12 to 30 carbon atoms, preferably 12 to 24, more preferably 12 to 18. Preferably, R<sup>11</sup> is a linear or slightly branched alkyl group and R<sup>12</sup> advantageously represents a hydrocarbonyl group with from 1 to 30 carbon atoms when monovalent, preferably with 6 or greater, more preferably 10 or greater, preferably up to 24, more preferably up to 18 carbon atoms. Preferably, R<sup>12</sup>, when monovalent, is a linear or slightly branched alkyl group. When R<sup>12</sup> is divalent, it is preferably a methylene or ethylene group. By "slightly branched" is meant having a single methyl branch.

The comb polymer may contain units derived from other monomers if desired or required, examples being CO, vinyl acetate and ethylene. It is within the scope of the invention to include two or more different comb copolymers.

The comb polymers may, for example, be copolymers of maleic anhydride or fumaric acid and another ethylenically unsaturated monomer, e.g. an  $\alpha$ -olefin or an unsaturated ester, for example, vinyl acetate as described in EP-A-214,786. It is preferred but not essential that equimolar amounts of the comonomers be used although molar proportions in the range of 2 to 1 and 1 to 2 are suitable. Examples of olefins that may be copolymerized with e.g. maleic anhydride, include 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and styrene. Other examples of comb polymer include methacrylates and acrylates.

The copolymer may be esterified by any suitable technique and although preferred it is not essential that the maleic anhydride or fumaric acid be at least 50% esterified. Examples of alcohols which may be used include n-dodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, and n-octadecan-1-ol. The alcohols may also include up to one methyl branch per chain, for example, 1-methylpentadecan-1-ol, 2-methyltridecan-1-ol as described in EP-A-213,879. The alcohol may be a mixture of normal and single methyl branched alcohols. It is preferred to use pure alcohols rather than alcohol mixtures such as may be commercially available; if mixtures are used the

tetradecene-1 and n-hexadecene-1 (for example, as described in WO9319106. Preferably, the number average molecular weight measured by Gel Permeation Chromatography against polystyrene standards of such a copolymer is for example, up to 30,000 or up to 40,000. The hydrocarbon copolymers may be prepared by methods known in the art, for example using a Ziegler type catalyst. Such hydrocarbon polymers may for example have an isotacticity of 75% or greater.

- (ii) Such compounds comprise an ester, ether, ester/ether compound or mixtures thereof in which at least one substantially linear alkyl group having 10 to 30 carbon atoms is connected via an optional linking group that may be branched to a non-polymeric residue, such as an organic residue, to provide at least one linear chain of atoms that includes the carbon atoms of said alkyl groups and one or more non-terminal oxygen, sulphur and/or nitrogen atoms. The linking group may be polymeric.

By "substantially linear" is meant that the alkyl group is preferably straight chain, but that straight chain alkyl groups having a small degree of branching such as in the form of a single methyl group branch may be used.

Preferably, the compound has at least two of said alkyl groups when the linear chain may include the carbon atoms of more than one of said alkyl groups. When the compound has at least three of said alkyl groups, there may be more than one of such linear chains, which chains may overlap. The linear chain or chains may provide part of the linking group between any two such alkyl groups in the compound.

The oxygen atom or atoms, if present, are preferably directly interposed between carbon atoms in the chain and may, for example, be provided in the linking group, if present, in the form of a mono- or poly-oxyalkylene group, said oxyalkylene group preferably having 2 to 4 carbon atoms, examples being oxyethylene and oxypropylene.

As indicated the chain or chains include carbon, oxygen, sulphur and/or nitrogen atoms.



polyoxypropylene glycol) may be tolerated but it is preferred that the glycol should be substantially linear.

5        Suitable glycols generally are substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having a molecular weight of about 100 to 5,000, preferably about 200 to 2,000. Esters are preferred and fatty acids containing from 10 to 30 carbon atoms are useful for reacting with the glycols to form the ester additives, it being preferred to use C<sub>18</sub> to C<sub>24</sub> fatty acid, especially behenic acid. The esters may also be prepared by  
10        esterifying polyethoxylated fatty acids or polyethoxylated alcohols.

15        Polyoxyalkylene diesters, diethers, ether/esters and mixtures thereof are suitable as additives, diesters being preferred when the petroleum based component is a narrow boiling distillate, when minor amounts of monoethers and monoesters (which are often formed in the manufacturing process) may also be present. It is important for active performance that a major amount of the dialkyl compound is present. In particular, stearic or behenic diesters of polyethylene glycol, polypropylene glycol or polyethylene/polypropylene glycol mixtures are preferred.

20        Other suitable esters are those obtainable by the reaction of

- (i)        an aliphatic monocarboxylic acid having 10 to 40 carbon atoms, and
- 25        (ii)        an alkoxyated aliphatic monohydric alcohol, wherein the alcohol has greater than 18 carbon atoms prior to alkoxylation and wherein the degree of alkoxylation is 5 to 30 moles of alkylene oxide per mole of alcohol.

30        The ester may be formed from a single acid reactant (i) and single alcohol reactant (ii); or from mixtures of acids (i) or alcohols (ii) or both. In the latter cases, a mixture of ester products will be formed which may be used without separation if desired, or separated to give discrete products before use.

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carbon number prior to alkoxylation should be above 18 and preferably within the preferred ranges recited above. Preferably, the individual alcohols in the mixture should not differ by more than 4 carbon atoms.

5 The esterification can be conducted by normal techniques known in the art. Thus, for example one mole equivalent of the alkoxyated alcohol is esterified by one mole equivalent of acid by azeotrope in toluene at 110-120°C in the presence of 1 weight percent of p-toluene sulphonic acid catalyst until esterification is complete, as judged by Infra-Red Spectroscopy and/or reduction of the hydroxyl and acid numbers.

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The alkoxylation of the aliphatic alcohol is also conducted by well-known techniques. Thus for example a suitable alcohol is (where necessary) melted at about 70°C and 1 wt % of potassium ethoxide in ethanol added, the mixture thereafter being stirred and heated to 100°C under a nitrogen sparge until ethanol ceases to be distilled off, the mixture subsequently being heated to 150°C to complete formation of the potassium salt. The reactor is then pressurised with alkylene oxide until the mass increases by the desired weight of alkylene oxide (calculated from the desired degree of alkoxylation). The product is finally cooled to 90°C and the potassium neutralised (e.g. by adding an equivalent of lactic acid).

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(iii) The non-ethylene hydrocarbon polymer may be an oil-soluble hydrogenated block diene polymer, comprising at least one crystallizable block, obtainable by end-to-end polymerisation of a linear diene, and at least one non-crystallizable block, the non-crystallizable block being obtainable by 1,2-configuration polymerisation of a linear diene, by polymerisation of a branched diene, or by a mixture of such polymerisations.

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**The additive concentrate composition (second aspect of the invention)**

- 5 The concentrate comprises either the additive as defined above, or (a), (b) and (c) as defined above, in admixture with a compatible solvent therefor.

Concentrates comprising the additive in admixture with a carrier liquid (e.g. as a solution or a dispersion) are convenient as a means for incorporating the additive  
10 into bulk oil such as distillate fuel, which incorporation may be done by methods known in the art. The concentrates may also contain other additives as required and preferably contain from 3 to 75 wt %, more preferably 3 to 60 wt %, most preferably 10 to 50 wt % of the additives preferably in solution in oil. Examples of  
15 carrier liquid are organic solvents including hydrocarbon solvents, for example petroleum fractions such as naphtha, kerosene, diesel and heater oil; aromatic hydrocarbons such as aromatic fractions, e.g. those sold under the 'SOLVESSO' tradename; alcohols and/or esters; and paraffinic hydrocarbons such as hexane and pentane and isoparaffins. The carrier liquid must, of course, be selected  
20 having regard to its compatibility with the additive and with the oil.

- 20 The additives of the invention may be incorporated into bulk oil by other methods such as those known in the art. If co-additives are required, they may be incorporated into the bulk oil at the same time as the additives of the invention or at a different time.

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**The fuel oil composition (third aspect of the invention)**

- 30 The fuel oil composition comprises either the additive or concentrate composition defined above, or (a), (b) and (c) as defined above, in admixture with a major proportion of fuel oil.

Vegetable oils are mainly triglycerides of monocarboxylic acids, e.g. acids containing 10-25 carbon atoms and have the following formula:



10 where R is an aliphatic radical of 10-25 carbon atoms which may be saturated or unsaturated.

Generally, such oils contain glycerides of a number of acids, the number and kind varying with the source vegetable of the oil.

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Examples of oils are rapeseed oil, coriander oil, soyabean oil, cottonseed oil, sunflower oil, castor oil, olive oil, peanut oil, maize oil, almond oil, palm kernel oil, coconut oil, mustard seed oil, beef tallow and fish oils. Rapeseed oil, which is a mixture of fatty acids partially esterified with glycerol, is preferred as it is available in large quantities and can be obtained in a simple way by pressing from rapeseed.

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Examples of derivatives thereof are alkyl esters, such as methyl esters, of fatty acids of the vegetable or animal oils. Such esters can be made by transesterification.

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As lower alkyl esters of fatty acids, consideration may be given to the following, for example as commercial mixtures: the ethyl, propyl, butyl and especially methyl esters of fatty acids with 12 to 22 carbon atoms, for example of lauric acid, myristic acid, margaric acid, palmitic acid, palmitoleic acid, stearic acid, oleic acid, elaidic acid, petroselic acid, ricinoleic acid, elaeostearic acid, linoleic acid, linolenic acid, eicosanoic acid, gadoleic acid, docosanoic acid or erucic acid, which have an iodine number from 50 to 150, especially 90 to 125. Mixtures with

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the additives of the invention in order to achieve the properties required by specification or customer applications. Such fuel production processes and methods also provide the refiner or fuel producer with the possibility of cost savings, allowing the diversion of better-performing but more expensive fuel streams into higher-profit applications whilst maintaining adequate fuel quality through the use of performance-enhancing additives.

In one use aspect of the invention, component (b) may be used in fuel compositions already containing (a) and (c) particularly in order to reduce the problem of CFPP regression but also (or alternatively) to improve fuel wax anti-settling performance and/or lubricity performance. Alternatively, (b) may be used in additive compositions comprising (a) and (c) in order to provide the same technical advantages upon addition of the combination of additives to the fuel.

In a further use aspect of the invention, the additive or concentrate, or (a), (b) and (c), is used in fuel oil preferably to improve low temperature properties (especially low temperature filterability performance), and/or lubricity performance and/or wax anti-settling performance of the fuel.

In the process, method, use and other aspects of the invention, the preferred embodiments of (a), (b) and (c) are those as described under the additive composition aspects of the invention.

The invention will now be described by means of example only as follows:

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#### Example 1: Avoidance of CFPP regression

A commercial winter diesel fuel 1, obtained from a service station in the Netherlands and already treated with ethylene-vinyl ester copolymers to improve fuel CFPP, was further treated with a wax anti-settling additive C and co-additives B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub> and B<sub>4</sub> according to this invention, to give the results shown in Table 1.

Fuel 1 had the following characteristics:

Cloud point

-7°C

Experiment No.	(a) EVA	Additives			(c) Additive C in ppm (w/w)	CFPP (°C)	CFPP Regression (°C)
1	present	None			none	-20°C	N/A
2	present	None			50	-18°C	2°C
3	present	None			75	-11°C	9°C
4	present	None			100	-11°C	9°C
		B1	B2	B3			
5	present	B4			50	-22°C	-2°C
6	present	50	50		50	-24°C	-4°C
7	present			50	50	-27°C	-7°C
8	present				50	-27°C	-7°C
		50					
9	present	50			75	-15°C	5°C
10	present		50		75	-22°C	-2°C
11	present			50	75	-24°C	-4°C

As seen from Table 1, the combination of EVA copolymer and wax anti-settling additive C showed significant CFPP regression of up to 9°C. In contrast, inclusion of co-additives B<sub>1</sub> to B<sub>4</sub> inclusive gave enhanced CFPP results when used with additive C at 50 ppm. Similarly, additives B<sub>2</sub> to B<sub>3</sub> gave enhanced CFPP at 75 ppm of Additive C (in the right hand column, a negative CFPP regression indicates enhanced CFPP). B<sub>1</sub>, when used with 75 ppm of Additive C, reduced the regression from 9°C (experiment 3) to 5°C (experiment 9), i.e. a 4°C improvement in fuel performance.

### Example 2: Enhancement of wax anti-settling performance

A second diesel fuel 2 also treated with ethylene vinylester copolymer additives to reduce CFPP was further treated with the same additives, the results being shown in Table 2.

Table 2 - CFPP and wax antisetling results in Fuel 2

Experiment No.	Additives			CFPP (°C)	% Wax Settled at 10°C below Cloud Point
	(a) ethylene copolymer	(c) Additive C in ppm (w/w)	(b) Additive B in ppm (w/w)		
12	present	none	None	-16°C	10

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18	-	-	622
19	-	150 ppm	557
20	75 ppm	75 ppm	434
21	150 ppm	-	531

The combination of C and B<sub>5</sub> improved lubricity performance, at same total treat rate, when compared with either component above.

6. The composition of claim 5, wherein (c) comprises at least one amine salt and/or amide of a mono- or polycarboxylic acid or reactive equivalent thereof.
- 5 7. The composition of claim 6, wherein (c) comprises one or more amides and/or amine salts, or mixtures thereof, of aromatic or aliphatic polycarboxylic acids or reactive equivalents thereof and alkyl- or dialkylamines.
- 10 8. The composition of any preceding claims, wherein the reactant (ii) comprises at least one aliphatic hydrocarbyl-substituted phenol.
9. The composition of any preceding claim, wherein (b) is combined with at least one amine bearing at least one hydrocarbyl substituent.
- 15 10. The composition of claim 9, wherein (b) is reacted with at least one amine to form the amine salt derivative thereof.
- 20 11. The composition of any preceding claim, wherein (b) comprises the product obtainable by the reaction between (i), (ii) and a further reactant (iii), wherein:  
(iii) comprises at least one compound comprising one or more aromatic moieties bearing at least one substituent  $-XR^1$  and at least one further substituent  $-R^3$ , wherein:  
25 X represents oxygen or sulphur,  
 $R^1$  represents hydrogen or a moiety bearing at least one hydrocarbyl group; and  $R^3$  represents a group selected from the list  $-COOH$ ,  $-SO_3H$  or a derivative thereof;  
and wherein X and  $R^1$  in reactants (ii) and (iii) may be the same or different.
- 30 12. The composition of claim 11 wherein the reactant (iii) comprises salicylic acid or at least one substituted derivative thereof.
13. The composition of claim 11 or 12 when read with claim 9 or 10.
- 35 14. The composition of claim 13, wherein (b) is the reaction product of (i) formaldehyde or a reactive equivalent thereof, (ii) at least one alkyl phenol,



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23. The additive composition obtainable by admixture of (b) and (c) as defined in claim 1.
24. The use of the composition of claim 23 in a fuel oil.
- 5 25. A fuel oil composition comprising fuel oil and either the composition of claim 23, or (b) and (c) as defined in claim 1.

# INTERNATIONAL SEARCH REPORT

International Application No

PCI/EP 99/03306

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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